JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.9b05280 • Publication Date (Web): 08 Jul 2019

Force-Dependent Multicolor Mechanochromism from a Single Mechanophore

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Supporting Information Placeholder

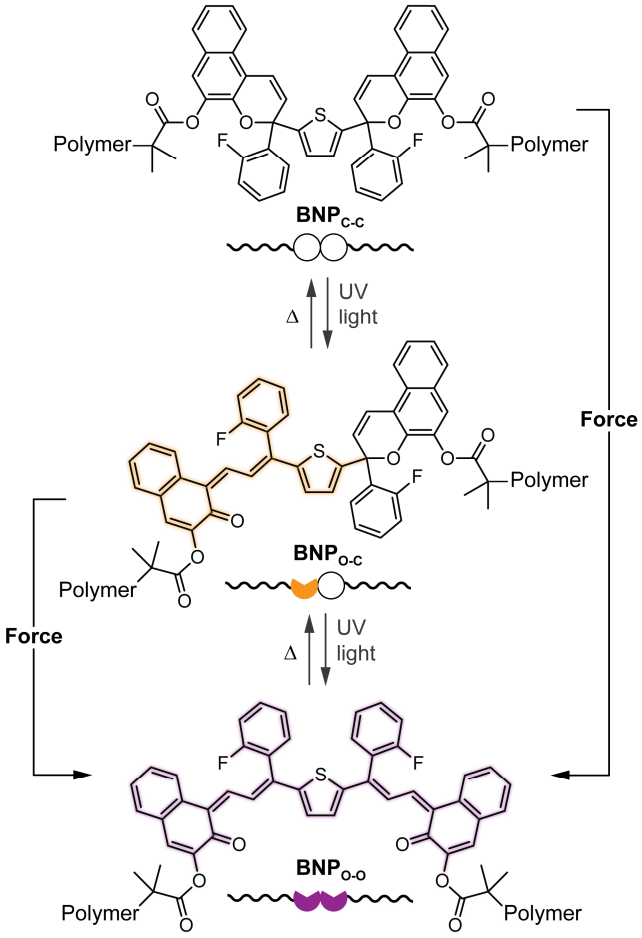
ABSTRACT: We report a bis-naphthopyran mechanophore that exhibits force-dependent changes in visible absorption. A series of polymers incorporating a chain-centered bis-naphthopyran mechanophore are activated using ultrasonication. By varying the length of the polymer chains, the force delivered to the mechanophore is modulated systematically. We demonstrate that the relative distribution of two distinctly colored merocyanine products is altered predictably with different magnitudes of applied force, resulting in gradient multicolor mechanochromism. The mechanochemical reactivity of bis-naphthopyran is supported by DFT calculations and described by a theoretical model that provides insight into the force-color relationship.

Mechanophores are molecules that undergo specific and productive chemical transformations under mechanical stress.[1] In polymer mechanochemistry, force is transduced to a mechanophore through covalently linked polymer chains.[2] Mechanophores that exhibit changes in color or luminescence, for example, enable the straightforward visible detection of stress and/or strain in polymers and polymeric materials.[3] A diverse library of mechanochromic molecular force probes has emerged including spiropyran[4] and naphthopyran,[5] which undergo 6π electrocyclic ring-opening reactions under force to generate colored merocyanine dyes. In addition, mechanophores that homolytically cleave to generate colored radical species,[6] the force-activated unzipping of polyladderene to form conjugated polyacetylene,[7] and the ring-opening reaction of rhodamine[8] have also been recently reported.

The development of mechanochromic mechanophores that are capable of distinguishing between different magnitudes of force through discrete visual signals remains an important challenge. Spiropyran[4d,9] and rhodamine[8b] exhibit a unique color transition in materials under active stress and after relaxation due to presumed changes in cis–trans isomerization and conformational torsion, respectively. Furthermore, taking advantage of the unique properties of phase-separated polymer and composite materials, differential activation of two different mechanochromic mechanophores introduced into hard and soft domains has been demonstrated under varying degrees of mechanical stimulation.[10] A single mechanophore, however, that is capable of achieving a force-dependent, gradient multicolor response is a desirable target.

We were intrigued by reports of multicolor photochromism in bis-naphthopyran (BNP) chromophores (Scheme 1).[11] The two pyran rings, which are initially in the closed-closed state ($BNP_{C\text{-}C}$), open sequentially under extended irradiation with UV light to generate distinctly colored merocyanine dyes. A single ring-opening reaction produces the open-closed form ($BNP_{O\text{-}C}$)

Scheme 1. Electrocyclic reactions of bis-naphthopyran produce distinctly colored merocyanine products via photochemical, thermal, and mechanochemical processes.



with absorption properties characteristic of typical merocyanine dyes; however, the ring-opening reaction of the second pyran unit generates the open-open bis-merocyanine species ($BNP_{O\text{-}O}$) that absorbs at longer wavelengths due to conjugation through the thiophene linker. Here, we report the mechanochemical reactivity of a BNP mechanophore that exhibits force-dependent multicolor mechanochromism. Interestingly, the mechanochemical behavior of the BNP mechanophore is distinct from its photochemical reactivity. In contrast to the sequential ring-opening behavior with light, $BNP_{O\text{-}O}$ appears to be generated directly with force. A dy-

namic equilibrium is achieved under mechanical activation in which the distribution of merocyanine products is increasingly biased toward $BNP_{O\text{-}O}$ with greater force applied to the BNP mechanophore. The trend in mechanochemical reactivity is described by a mechanistic model that captures the experimentally determined force-color relationship.

Density functional theory (DFT) calculations using the easily implemented constrained geometries simulate external force (CoGEF) method[12] were initially performed to evaluate the mechanochemical activity of bis-naphthopyran (see the Supporting Information (SI) for details). Encouragingly, the calculations predict successful ring-opening reactions of both pyran units upon molecular elongation. To experimentally evaluate the mechanochemical reactivity of bis-naphthopyran, we synthesized a series of poly(methyl acrylate) (PMA) polymers incorporating a BNP unit near the center of the polymer chain (Scheme 2). An *ortho*-fluorophenyl group was incorporated into the BNP structure, which reduces the rate of thermal ring-closure and extends the lifetime of the merocyanine species.[13] Polymers with number average molecular weights (M_n) in the range 22–330 kDa were prepared (Table 1) and mechanically activated in solution using ultrasonication, which generates elongational forces on polymer chains that are maximized near the chain midpoint. According to the bead–rod model, the force experienced by a polymer under these conditions is dependent upon the length of the chain.[14] Thus, the magnitude of force applied to a BNP molecule during ultrasonication is tuned by varying the degree of polymerization (DP) of the attached polymer chains, with longer polymers transducing greater force. Accordingly, the activation rate of mechanochemical reactions is directly proportional to DP above a threshold chain length.[12b] Although DP is a better descriptor of mechanical activation,[15] we refer to polymer molecular weight as a more identifiable metric since only PMA was used in this study.

Scheme 2. Synthesis of poly(methyl acrylate) polymers containing a chain-centered bis-naphthopyran unit.

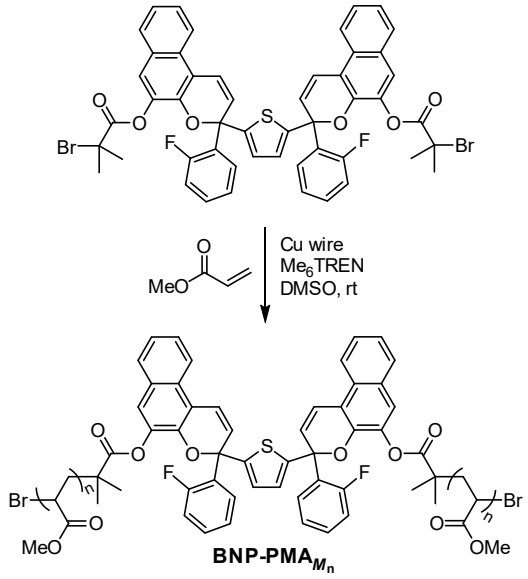


Table 1. Polymer characterization and quantification of force-dependent mechanochromism.

Polymer	M_n (kDa)[a]	DP[b]	$Đ$[a]	B_{620}/B_{460}[c]
$BNP\text{-}PMA_{22}$	21.5	250	1.19	0.24 ± 0.010
$BNP\text{-}PMA_{40}$	40.0	465	1.10	0.32 ± 0.025
$BNP\text{-}PMA_{53}$	53.1	617	1.10	0.40 ± 0.033
$BNP\text{-}PMA_{73}$	73.2	850	1.10	0.44 ± 0.014
$BNP\text{-}PMA_{98}$	97.6	1130	1.20	0.51 ± 0.068
$BNP\text{-}PMA_{165}$	165	1920	1.15	0.62 ± 0.047
$BNP\text{-}PMA_{330}$	330	3830	1.24	0.75 ± 0.024

[a]Determined from GPC-MALLS. [b]M_n/M_0. [c]Average values from absorbance data fitted to eq 1. Standard deviation from a minimum of three trials.

The photochromic properties of a 330 kDa polymer containing a chain-centered bis-naphthopyran molecule (**$BNP\text{-}PMA_{330}$**) were initially investigated and compared to its mechanochemical reactivity. Photochemical and mechanochemical reactions were monitored in real-time by UV-vis absorption spectroscopy using a peristaltic pump to continuously circulate a polymer solution between a reaction vessel and a UV-vis flow cell.[15a] A THF solution of **$BNP\text{-}PMA_{330}$** at −45 °C was irradiated with UV light (λ = 311 nm) and absorption spectra were acquired over time (Figure 1a). At early irradiation times, a new peak with an absorption maximum at approximately 460 nm emerges, corresponding to the $BNP_{O\text{-}C}$ species.[11a] A longer wavelength absorption signal appears after extended UV irradiation that corresponds to the $BNP_{O\text{-}O}$ form. To better characterize the formation of each species over time, the absorbance at two characteristic wavelengths of 460 nm and 620 nm were monitored continuously. The latter wavelength was chosen to minimize overlap with the absorption of $BNP_{O\text{-}C}$, allowing for the selective detection of $BNP_{O\text{-}O}$. Under constant photoirradiation of **$BNP\text{-}PMA_{330}$**, the absorbance at 460 nm increases rapidly and reaches a maximum well before the absorbance at 620 nm. These observations are consistent with a sequential photoactivation mechanism in which $BNP_{C\text{-}C}$ undergoes a single ring-opening reaction to generate $BNP_{O\text{-}C}$, followed by transformation of the second pyran ring to produce $BNP_{O\text{-}O}$. Tracking the concentration of each species as a function of photoirradiation time using extinction coefficients estimated from similar isolated small molecules[11a,b] further supports this mechanism (Figure S1).

Mechanochemical activation of PMA chain-centered bis-naphthopyran was investigated by subjecting polymers in THF at −45 °C to continuous ultrasonication (8.2 W/cm^2) using the same analytical flow setup employed in the photoirradiation experiments. In contrast to the sequential photoactivation behavior, mechanochemical activation of **$BNP\text{-}PMA_{330}$** occurs via a different mechanism (Figure 1b). The absorbance at 620 nm reaches a maximum value early, while the absorbance at 460 nm continues to increase more slowly with longer ultrasonication exposure. These data indicate that $BNP_{O\text{-}O}$ is formed relatively quickly in the mechanochemical reaction compared to $BNP_{O\text{-}C}$, which is generated relatively slowly. Ultrasound-induced mechanical activation of lower molecular weight **$BNP\text{-}PMA_{40}$** under the same conditions exhibits a similar trend in absorbance over time with the population of $BNP_{O\text{-}O}$ reaching a steady state before $BNP_{O\text{-}C}$; however, the absorption spectra are markedly different (Figure 1c). Remarkably, these results suggest that the relative distribution of $BNP_{O\text{-}C}$ and $BNP_{O\text{-}O}$ resulting from the mechanochemical reaction and the correlated visible absorption spectrum are force-dependent (*vide infra*). Control experiments performed on a chain-end functional polymer confirm the mechanical origin of the observed ultrasound-induced reactivity (Figure S2).

To further quantify how varying force affects the dynamic equilibrium of the system and the distribution of merocyanine species at the mechanostationary state,[15a] the series of polymers was subjected to ultrasound-induced mechanical activation as described above, the absorbance at 460 nm and 620 nm was plotted as a function of sonication time, and the curves were fitted to eq 1:

$$Abs(t) = B(1 - e^{-kt}) \quad (1)$$

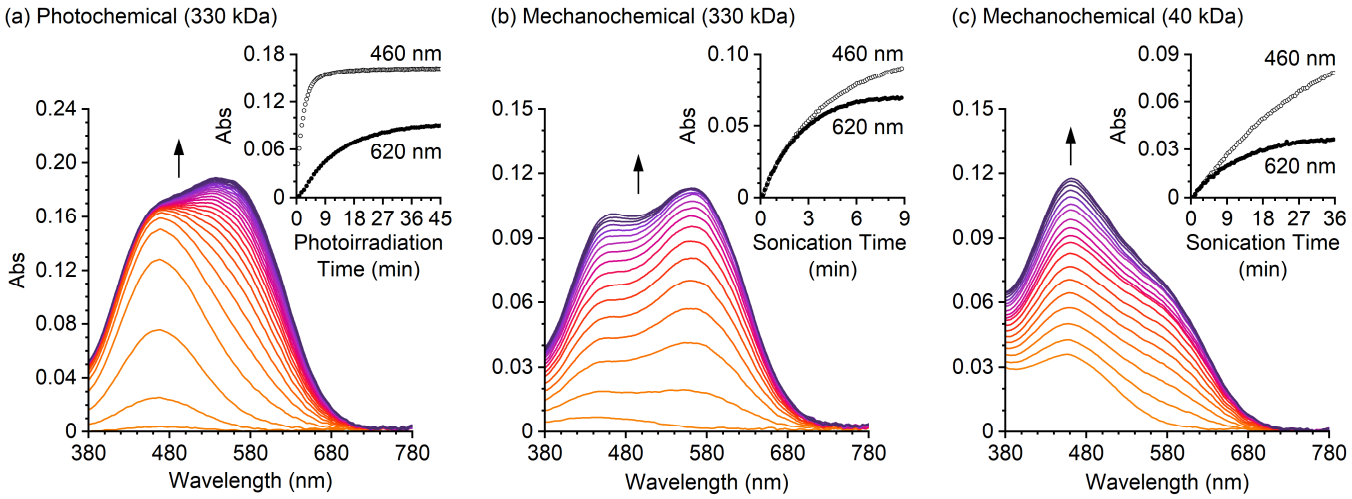


Figure 1. UV-vis absorption behavior of bis-naphthopyran under photochemical and mechanochemical activation. (a) Absorption spectra of 330 kDa **BNP-PMA$_{330}$** upon increasing exposure to UV light (λ = 311 nm) illustrating sequential ring-opening behavior. Insets show absorbance monitored at characteristic wavelengths of 460 nm and 620 nm during the reactions. UV-vis absorption behavior of (b) 330 kDa **BNP-PMA$_{330}$** and (c) 40 kDa **BNP-PMA$_{40}$** subjected to ultrasound-induced mechanochemical activation demonstrating a non-sequential ring-opening process and force-dependent visible absorption. Polymer concentrations are 2 mg/mL in THF.

where *Abs(t)* is the absorbance at a specific wavelength at time *t*, *B* is the amplitude (the maximum absorbance value), and *k* is the effective rate constant. A representative example is illustrated in Figure 2a. Average values of *B* measured at 460 nm (B_{460}) and 620 nm (B_{620}) were determined from a minimum of three trials for each polymer and are reflective of the steady-state concentration of merocyanine species. More importantly, as discussed below, the ratio of B_{620} to B_{460} for each polymer provides a consistent measure of the ensemble average steady-state distribution of BNP$_{O\text{-}C}$ and BNP$_{O\text{-}O}$ at a particular applied force (Table 1).

Representative traces of absorbance at 620 nm scaled to respective values of B_{460} as a function of sonication time are shown for each polymer in Figure 2b. These data reveal how the populations of merocyanine species change over time to reach a steady-state concentration of BNP$_{O\text{-}C}$ and BNP$_{O\text{-}O}$. The relative spectral contribution from the BNP$_{O\text{-}O}$ state becomes greater with increasing molecular weight of the attached polymers, and thus with greater force applied to the BNP mechanophore. Additionally, the steady-state concentration of BNP$_{O\text{-}O}$ is reached faster with higher molecular weight polymers, which is consistent with longer chains being activated more quickly in mechanochemical reactions.

We constructed a theoretical model to further understand the force-color relationship observed for the BNP mechanophore (Figure 2c). As mentioned above, the average ratio of B_{620}/B_{460} determined for each polymer serves as a proxy to describe the overall distribution of BNP$_{O\text{-}C}$ and BNP$_{O\text{-}O}$ resulting from the mechanochemical reaction. In the model, the relative steady-state concentrations (φ) of BNP$_{O\text{-}C}$ and BNP$_{O\text{-}O}$ given by eq 2:

$$\varphi_{O\text{-}O} = 1 - \varphi_{O\text{-}C} = \frac{[BNP_{O\text{-}O}]}{[BNP_{O\text{-}C}] + [BNP_{O\text{-}O}]} \quad (2)$$

are related to M_n according to eq 3:

$$\varphi_{O\text{-}O} = 1 - e^{-c(M_n/M_0)} \quad (3)$$

where *c* is a constant and M_0 is the molecular weight of the monomer unit (DP = M_n/M_0). The concentration of each merocyanine species can be calculated from the experimentally determined absorbance values at 460 nm and 620 nm using the Beer-Lambert relationship and previously estimated extinction coefficients to predict the dependence of B_{620}/B_{460} on M_n (see the SI for details). The goal of this model is not to describe the system exactly, but rather capture the overall trend observed for the changes in visible absorption resulting from mechanical activation of BNP with

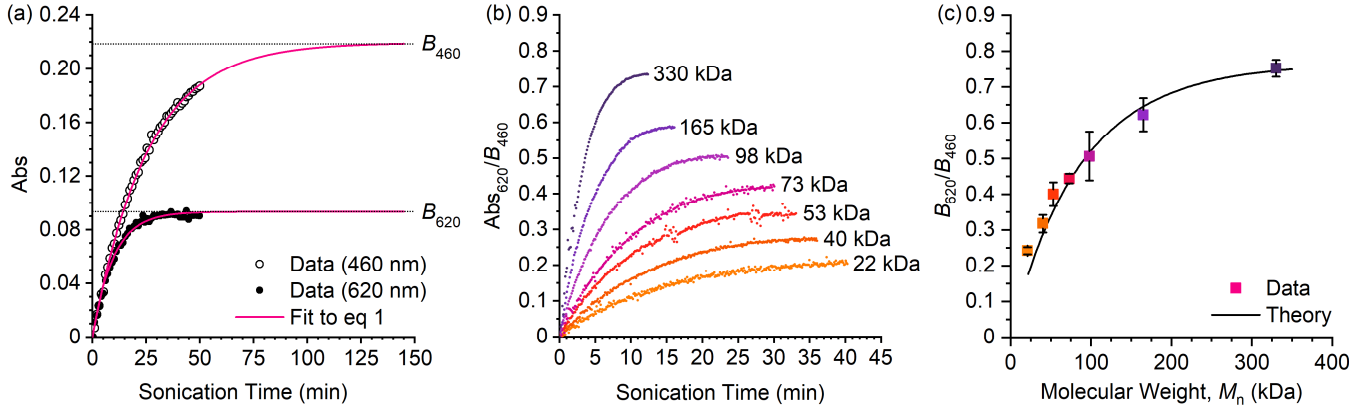


Figure 2. Evaluation of force-dependent mechanochromism of the BNP mechanophore. (a) Representative kinetic plots for **BNP-PMA$_{73}$** demonstrating the determination of steady-state absorbance values. Absorbance at 460 nm and 620 nm was recorded for each polymer during ultrasound-induced mechanical activation and fitted to eq 1 to calculate B_{460} and B_{620}. (b) Representative traces of absorbance at 620 nm as a function of sonication time for each polymer scaled to their respective values of B_{460}. (c) Ratios of B_{620}/B_{460} determined for polymers of varying M_n describe the overall distribution of BNP$_{O\text{-}C}$ and BNP$_{O\text{-}O}$ and are consistent with a theoretical model that predicts the force-color relationship.

varying force. This simple model is in good agreement with the data.

The experimental results presented above demonstrating force-dependent, gradient multicolor mechanochromism of the BNP mechanophore are consistent with a non-sequential activation mechanism in which $BNP_{C\text{-}C}$ is converted directly to $BNP_{O\text{-}O}$ (see the SI for details). Biased by external force, $BNP_{C\text{-}C}$ exists in equilibrium with $BNP_{O\text{-}C}$ and $BNP_{O\text{-}O}$ and the distribution of the two merocyanine species is dictated by the balance between the forward rate of mechanochemical activation and thermal electrocyclization, resulting in a mechanostationary state. Although the complex interconversion processes preclude an exact solution of the rate law, numerical modeling supports the proposed mechanism and suggests that $BNP_{O\text{-}C}$ is produced predominately, if not exclusively, from thermal electrocyclization of $BNP_{O\text{-}O}$. The data and the kinetic model also indicate that $BNP_{O\text{-}C}$ can be activated mechanochemically to regenerate $BNP_{O\text{-}O}$. As the average DP, or M_n, of the polymers attached to the BNP mechanophore increases, the rate of electrocyclic ring-opening increases, which shifts the merocyanine distribution at the mechanostationary state toward $BNP_{O\text{-}O}$. This feature is reflected in a greater spectral contribution from $BNP_{O\text{-}O}$ relative to $BNP_{O\text{-}C}$ and a larger ratio of B_{620}/B_{460}. This mechanism also accounts for the more rapid mechanochemical generation of $BNP_{O\text{-}O}$ compared to $BNP_{O\text{-}C}$. With the exception of **BNP-PMA$_{22}$**, polymer chain scission occurs with extended ultrasonication as expected, leading to irreversible loss of $BNP_{O\text{-}O}$. This degradation pathway is included explicitly in the kinetic model; however, it appears to have a minimal effect on the value of B_{620}/B_{460}.

In summary, we have developed a bis-naphthopyran (BNP) mechanophore that exhibits force-dependent, gradient multicolor mechanochromism. The BNP mechanophore was incorporated into a series of polymers with different degrees of polymerization and mechanically activated in solution using ultrasonication. By changing the length of the attached polymer chains, the amount of force delivered to the mechanophore was varied systematically. Mechanical activation of BNP proceeds via a mechanistically distinct pathway compared to the photochemical process. Increasing the force applied to the BNP mechanophore predictably alters the relative distribution of two distinctly colored merocyanine products, resulting in a graded change in the overall visible absorption spectrum. The mechanochemical behavior of the BNP mechanophore is described by a theoretical model that provides insight into the force-color relationship.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and additional characterization data, kinetic modeling, synthetic procedures, DFT calculations, GPC chromatograms, UV-vis data, and NMR spectra (PDF).

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Financial support from Caltech and the Dow Next Generation Educator Fund is gratefully acknowledged. We thank Corey Husic, Anna Overholts, and Dr. Scott Virgil for helpful discussions and the Caltech Center for Catalysis and Chemical Synthesis of the Beckman Institute at Caltech for access to equipment. MEM was supported by a NSF Graduate Research Fellowship (DGE-1745301).

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